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## Detection of oxygen traces in nitrogen and hydrogen-rich atmosphere

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### Abstract

Tin oxide sensors are evaluated to detect traces of oxygen in the range 0–100 ppm both in nitrogen and hydrogen (4.5 vol% H<sub>2</sub> in N<sub>2</sub>) atmospheres. In nitrogen, significant relative responses to oxygen are measured at 623 K and 723 K. However, at lower temperature, 523 K, the response strongly decreases. In the presence of hydrogen, on the contrary, interesting responses are measured at 523 K. At higher temperature, 623 K and 723 K, on one hand SnO<sub>2</sub> sensors begin to reduce, and on the other hand, oxygen is partly consumed by reaction with hydrogen. Oxygen trace detection (5–100 ppm) is thus only possible in hydrogen atmosphere (4.5 vol% H<sub>2</sub>) at 523 K.

### Keywords:

*tin oxide, sensor, oxygen, hydrogen*

### Introduction

Today, the detection of gas traces (such as CO, O<sub>2</sub>, etc.) in atmospheres containing hydrogen is of great interest, in particular for fuel cells application [1], [2] and [3]. Currently, several commercial sensors are dedicated to oxygen traces detection for various applications. Electrochemical probes offer a wide range of oxygen concentration detection, notably that of Figaro GS oxygen sensor, typically used as oxygen sensor in hydrogen-based atmosphere [4]. These electrochemical probes have the advantage to exhibit low cross-sensitivity to the hydrogen gas, which means that their oxygen response is not dependant on hydrogen content. However, they work at temperatures close to the ambient and cannot be used for in situ measurements with temperature ranging from 523 K to 723 K. In contrast, yttria-stabilized zirconia (YSZ) oxygen sensors must be used at high temperature ( $T > 873$  K) to insure a satisfactory electric conductivity of YSZ sensing material. However, they are also sensitive to hydrogen and to hydrocarbons because gas combustion in the presence of oxygen occurs locally in the neighborhood of the sensing element. Consequently, the detected quantity of oxygen is usually strongly underestimated by these sensors [5]. Sensors made of semiconducting materials have also been developed for the detection of oxygen in various gases as their electrical conductivity varies with the partial pressure of oxygen. Among them, zinc oxide and cerium oxide sensors, both n type semiconductors, have been studied. The former for measuring micro-concentration of oxygen (from 10<sup>-6</sup> vol% to 10<sup>-1</sup> vol%) presents good chemical stability, no sensitivity to hydrogen and can be used between 293 K and 1390 K. The latter has a sensitivity to O<sub>2</sub> coming from its non-stoichiometry that induces a good electrical mobility. Unfortunately, the possible effects of interfering gases, in particular hydrogen, on these sensors have not been clarified yet [6] and [7]. If it is indeed important to know the range of measured O<sub>2</sub> concentrations and the working temperatures, it is also

necessary to study and understand the behavior of the sensors, especially in terms of deterioration, in a gaseous atmosphere containing hydrogen [8] and [9]. While gas detection in ambient air has been the concern of many studies, the potentiality of oxygen traces detection by tin dioxide, the most widely used material for semiconductor gas sensor, as well as the stability of these sensors in nitrogen or with hydrogen (4.5 vol%, balanced in N<sub>2</sub>), have been scarcely studied and are the subject of this contribution. After a thermodynamic study of H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/O<sub>2</sub>/SnO<sub>2</sub> systems to determine the gas equilibrium concentrations and SnO<sub>2</sub> stability domain, experimental results with sensors are presented.

## Experimental

### SnO<sub>2</sub> sensor preparation

Sensing elements are constituted by a tin oxide thick film (2 mm × 4 mm) deposited by screen-printing (Aurel C890 machine) onto  $\alpha$ -alumina substrates (38.1 mm × 5.1 mm × 0.381 mm). The screen-printing ink was prepared with a home-made tin oxide paste. SnO<sub>2</sub> layers were annealed for 12 h at 1073 K (10° min<sup>-1</sup>) in air before being used. For electrical measurements purpose, two screen-printed gold electrodes (2 mm × 1 mm) with a thickness of about 1  $\mu$ m were also deposited from commercially available paste on the front side (Fig. 1).

### Test bench and experiment description

In this study, the sensors were directly placed in a tubular furnace, on a sample holder allowing electrical connections with gold wires. The sensor temperature was fixed by the furnace which constitutes the main part of the test bench. Measurements were performed at 523 K, 623 K and 723 K.

Experiments were carried out either in dry N<sub>2</sub> or in H<sub>2</sub>-N<sub>2</sub> atmospheres (4.5 vol% H<sub>2</sub>) to detect various oxygen concentrations ranging from 5 to 100 ppm. Three starting gas feeds were used: N<sub>2</sub> (impurities: [H<sub>2</sub>O] < 3 ppm, [O<sub>2</sub>] < 2 ppm and [C<sub>n</sub>H<sub>n</sub>] < 0.5 ppm), 10% H<sub>2</sub> balanced in N<sub>2</sub> (Air Liquide) and a homemade mixture of 2150 ppm of O<sub>2</sub> in N<sub>2</sub>. Mass flow meters (Brooks Instrument) monitored by computer (software ©Labview) were placed at the entrance of the furnace to control the concentrations of the different gases. The tests were made with a total gas flow of 5 l/h. Before starting the experiments, a primary vacuum was set in the bench in order to remove residual oxygen. However, it was difficult to reach concentrations lower than a few ppm (2–5). To limit the possible leaks, all the connections between the bench and the gas inlets were made of stainless steel and valves stop were positioned upstream to each flow meter. A SYSTECH Instrument 910 oxygen probe was placed at the exit of the furnace to control the oxygen concentration.

### Material characterization and sensor performance measurements

In order to analyse SnO<sub>2</sub> sensing element stability, X-ray diffraction analysis was carried out with a Siemens D 5000 diffractometer (Cu K $\alpha$  radiation, 1.5406 Å wavelength, with acquisition parameters of  $2\theta = 15-80^\circ$  and a step of 0.005°) on samples obtained after different tests at various temperatures and gaseous atmospheres.

The conductance “ $G$ ” (in S) of SnO<sub>2</sub> sensors was measured by a Keithley 6430 apparatus with two gold wires fixed on gold electrodes. To compare the sensor responses at different temperatures, the relative sensor response to oxygen at a fixed temperature  $T$  was defined by  $(G_o - G)/G$ , where  $G$  is the conductance of the sensor under target gas with oxygen (either in N<sub>2</sub> or N<sub>2</sub>-H<sub>2</sub> atmosphere) and  $G_o$  is the baseline conductance under oxygen free nitrogen or hydrogen carrier gas.

## Thermodynamic study

A thermodynamic study of the systems H<sub>2</sub>/O<sub>2</sub> and SnO<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub> was first performed to understand the reactivity of the system H<sub>2</sub>-O<sub>2</sub> and the stability of SnO<sub>2</sub> under the experimental conditions. Calculations were performed with ©Thermodata software (Thermodata-INPG-CNRS-Grenoble-France).

### System H<sub>2</sub>/O<sub>2</sub>

The reactivity of the system H<sub>2</sub>–O<sub>2</sub> with temperature was studied for oxygen contents of 5 ppm, 100 ppm,  $2.25 \times 10^4$  ppm and  $21 \times 10^4$  ppm in H<sub>2</sub> atmosphere (4.5 vol% balanced in N<sub>2</sub>). In the temperature range 300–1200 K, a total reaction is observed according to the equation:



All oxygen is consumed in the domain  $5\text{--}2.25 \times 10^4$  ppm. For example, in Fig. 2a with 5 ppm of O<sub>2</sub>, 10 ppm of H<sub>2</sub>O is produced, and in Fig. 2b, for an oxygen concentration of  $2.25 \times 10^4$  ppm in 4.5 vol% H<sub>2</sub>, the reaction is total: H<sub>2</sub> and O<sub>2</sub> are completely consumed and the concentration of H<sub>2</sub>O is 4.5 vol%. It is important to note that the thermodynamic study is realized in static and not dynamic environment, contrary to experimental study presented in part IV.

### System SnO<sub>2</sub>/H<sub>2</sub>/O<sub>2</sub>

The variation of the reduction temperature of SnO<sub>2</sub> in H<sub>2</sub> (4.5 vol%)–N<sub>2</sub> atmosphere was studied in our experimental conditions. Following the reaction (1) one may write:



Results are presented in Fig. 3a and b. For an oxygen concentration of 5 ppm (Fig. 3a), SnO<sub>2</sub> reduction is total from 400 K and the oxygen is completely consumed in all the temperature range. The temperature at which the reduction is total is shifted to 450 K for oxygen concentrations of 100 ppm with always an entire consumption of O<sub>2</sub>. The reduction is displaced towards higher temperatures because the environment becomes less reducing. Thus, with the highest oxygen content in our experiment (100 ppm), in the 523–723 K temperature range, a total reduction of SnO<sub>2</sub> to metallic Sn should be observed with a complete consumption of the oxygen initially introduced. To obtain a thermodynamic stability of SnO<sub>2</sub> in our conditions, at least 1000 ppm of oxygen in 4.5 vol% H<sub>2</sub> would be required as the reduction of tin dioxide begins only at around 700 K in these conditions (Fig. 3b). As a conclusion, in our conditions, 4.5 vol% H<sub>2</sub> balanced with N<sub>2</sub>, and O<sub>2</sub> concentration in the range of 0–100 ppm, a total consumption of oxygen according to reaction (1) and a total reduction of SnO<sub>2</sub> according to reaction (2) should be observed at thermodynamic equilibrium. However, our experiments (part IV) are conducted under continuous gas flow. Therefore, kinetics will defined the oxygen concentration and the reduction state of SnO<sub>2</sub>.

## Experimental results

### Calibration of the test bench

To calibrate the test bench, a SYSTECH Instrument probe was positioned at the exit of the furnace to measure the real oxygen concentration at the outlet, when we inject, at the inlet, concentrations in the range 0–100 ppm, either in N<sub>2</sub> or H<sub>2</sub> carrier gas. It was checked that the measurement of the oxygen concentration by the commercial probe was not significantly influenced by the nature of the carrier gas. Tests were carried out without and with a sensor inside the furnace in order to investigate if the presence of a sensor changes the oxygen concentrations measured at the outlet.

Measurements conducted at various temperatures are reported in Table 1. At 293 K, both in nitrogen or 4.5 vol% hydrogen, the oxygen concentrations measured by the electrochemical probe are similar to the injected ones. For low injected concentrations (0 and 5 ppm), the measurements of the probe are influenced by the residual oxygen content (4–6 ppm) in the test bench. This explains that measured values are higher than injected ones. For experiments performed in nitrogen, similar results were obtained for all temperatures in the range 293–723 K. On the contrary, with 4.5 vol% H<sub>2</sub>, at 523 K, a significant decrease of the values read by the probe is observed (for example 81 ppm for 100 ppm injected), which can be attributed to a significant oxygen consumption via reaction (1) in the furnace, in agreement with the

thermodynamic study. At 723 K, the probe does not detect significant oxygen concentration (4 ppm). When hydrogen flow is stopped and replaced by nitrogen (last 2 points in Table 1), the detected oxygen content tends to return to the injected value (100 ppm) with a slow kinetics (gas flow effect).

The same kind of tests was carried out with a SnO<sub>2</sub> sensor in the furnace, for 4.5 vol% H<sub>2</sub> atmosphere; results are presented in Table 2. The oxygen contents measured by the probe at the furnace exit are always smaller when a sensor is present (example at 523 K: 47 ppm with the sensor, compared to 81 ppm without the sensor, for 100 ppm injected). This phenomenon indicates a supplementary consumption of oxygen by the sensor itself, as a result of SnO<sub>2</sub> catalytic activity.

As a conclusion, in the temperature range 523–723 K and in the presence of 4.5 vol% of hydrogen, strong oxygen consumption occurs in the furnace, which is enhanced by the presence of a SnO<sub>2</sub> sensor. As a result, there is a high gradient of oxygen concentration between the injected values (inlet) and measured ones by the probe (outlet). The local oxygen concentration around the sensing layer cannot be accurately determined. Consequently, in the following sections of this paper, except if it is mentioned, the indicated oxygen concentration will be the injected ones at entrance of the bench.

#### Sensor tests in nitrogen carrier gas

In this part, performances of SnO<sub>2</sub> sensors were investigated at 523 K, 623 K and 723 K. For the first measurements at 523 K, oxygen concentrations of 5, 15, 30, 50 and 100 ppm are injected during 1 h. This cycle of injections was reproduced two times (Fig. 4). The sensor presents a good response to oxygen and conductance decreases with increasing O<sub>2</sub> concentration, according to the well-known detection mechanism of tin oxide sensors for oxidizing gas. Except a difference for the first injection of 5 ppm in initial cycle, explained by residual oxygen in inlet pipe, reproducible signals are measured.

Fig. 5 shows the dynamic electrical response of sensors in N<sub>2</sub> atmosphere for several injection cycles obtained at 623 K, for O<sub>2</sub> concentration in the range 5–100 ppm. Here again, except for the first cycle, the sensor responses are reproducible. Sensor responses at 623 K are higher than the ones obtained at 540 K; the conductance decreases more strongly with increasing O<sub>2</sub> concentration. The sensor responses obtained at 723 K are in the same conductance range as the one measured at 623 K.

Relative responses of the sensor expressed by  $(G_0 - G)/G$  are presented in Fig. 6, as a function of O<sub>2</sub> concentration and of temperature. High oxygen responses are observed at 623 K and 723 K in comparison to the ones at 523 K. Significant relative responses are measured, proving the potentialities of tin oxide sensors for detection of oxygen in the studied concentration range 5–100 ppm, in nitrogen carrier gas.

#### Sensor tests in the presence of H<sub>2</sub> (4.5 vol% in N<sub>2</sub>)

In this part, potentiality of SnO<sub>2</sub> sensors for the detection of oxygen traces in a hydrogenated environment is presented.

Responses at 523 K for three cycles of O<sub>2</sub> injection are shown in Fig. 7. The sensors present good responses with increasing sensibilities for increasing O<sub>2</sub> content (5, 30 and 100 ppm). As for previous test, excepted for the first injection of the initial cycle, responses are reproducible. The observed behavior is the same as in N<sub>2</sub> atmosphere. However, in nitrogen, the measured quantities of O<sub>2</sub> by the SYSTECH Instrument probe were close to those injected, contrary to what it is observed in a hydrogenated atmosphere. The values measured at the exit of the bench are 3, 12 and 47 ppm, respectively for nominal values at the entrance of 5, 30 and 100 ppm (Table 2). Moreover, at 523 K, SnO<sub>2</sub> begins to be reduced to metallic tin as proved by the light grey coloration of the sensing layer and in agreement with thermodynamic calculations [3]. Nevertheless, X-ray analysis of SnO<sub>2</sub> sensor layer after test at 523 K does not allow to detect any reduction phenomenon; besides characteristic peaks of alumina (sensor substrate) and gold (electrodes), only SnO<sub>2</sub> phase is observed. No metallic tin can be seen. Sensor responses measured at 623 K in 4.5 vol% H<sub>2</sub> as a function of time, for the same oxygen nominal injections as previously, 5, 30 and 100 ppm, are reported in Fig. 8. The



measurements are reproducible over three cycles. A significant response is still observed for 100 ppm O<sub>2</sub> injection, but the responses to 5 and 30 ppm injections are quite weak. No phase reduction of SnO<sub>2</sub> into metallic tin was observed by X-rays analysis in spite of a dark coloration of the sensing element. This means, that at 523 K and 623 K, a partial reduction of SnO<sub>2</sub> probably occurs, but it remains limited to the surface. At 723 K, the sensor presents no more sensitivity to oxygen. At the end of the measurement, the sensitive element became black. X-ray analysis confirms the degradation (reduction) of the tin dioxide sensing element. Tin (Sn) and tin oxide SnO can be observed as well as AuSn, compound resulting from reaction with gold electrodes. Alumina phase corresponds to the sensor substrate (Fig. 9). Relative responses measured both in nitrogen and 4.5 vol% hydrogen are summarized in Fig. 10. In order to compare the results, the indicated oxygen concentrations are the measured concentrations at the furnace outlet. It is important to remind that these outlet concentrations are similar to the injected ones for experiments in nitrogen. However, for hydrogen experiments, outlet measured values are strongly lowered as reported previously (Table 2). Especially, the oxygen content is close to 0 at 723 K, whatever the injected concentration is (5, 30 or 100 ppm).

In N<sub>2</sub> environment, significant relative response were obtained at 623 K and 723 K. At lower temperature, 523 K, the sensibility is quite low. In the presence of hydrogen, it emerges from Fig. 10 that at 523 K and 623 K, the sensitivities of the sensors to oxygen are quite more important than in nitrogen. At 723 K, no response is measured as oxygen is completely converted in the furnace. Furthermore, in agreement with the thermodynamic study showing a reduction of tin dioxide in metallic tin beginning at 380 K for 5 ppm of oxygen, the reduction of SnO<sub>2</sub> layer is confirmed by X-rays diffraction analysis at 723 K. The reduction of the sensitive element is also correlated to its change of coloration which changes from light grey (523 K) to black (723 K) in hydrogenated gas (4.5 vol% H<sub>2</sub>), while it remains white in all the studied domain of temperature under N<sub>2</sub>.

## Conclusion

The objective of this study was to estimate the potentialities of SnO<sub>2</sub> sensors to measure weak oxygen concentrations in the range of 5–100 ppm under N<sub>2</sub> or hydrogenated H<sub>2</sub> atmosphere, in the temperature range 523–723 K.

The test bench developed for this application allowed to control well the oxygen contents in the range 5–100 ppm and the temperature from 523 K to 723 K, but only under nitrogen. Under hydrogenated atmosphere, considering experimental conditions, an important oxygen conversion occurs in the furnace as predicted by the thermodynamic calculations.

In nitrogen, SnO<sub>2</sub> sensors are able to detect oxygen traces from 5 to 100 ppm with high sensitivity at 623 K and 723 K. In hydrogen, detection of oxygen was possible at 523 K and 623 K. However, the stability of SnO<sub>2</sub> sensors for a long term application is still questionable as we observed superficial reduction of the sensing element. Operating temperature should be decreased, preferably down to 523 K, to improve life duration of the sensor.

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## Figures captions

*Figure 1: Photograph of SnO<sub>2</sub> gas sensor developed by screen-printing on alumina substrate.*

*Figure 2: Gas composition (vol%) versus temperature at thermodynamic equilibrium of H<sub>2</sub>–O<sub>2</sub>–N<sub>2</sub> system with initial composition of 4.5 vol% H<sub>2</sub> and O<sub>2</sub> contents fixed at (a) 5 ppm and (b)  $2.25 \times 10^4$  ppm.*

*Figure 3: SnO<sub>2</sub>–Sn contents (mol%) versus temperature at thermodynamic equilibrium in 4.5 vol% H<sub>2</sub> balanced in N<sub>2</sub>, with O<sub>2</sub> contents fixed at (a) 5 ppm and (b)  $10^3$  ppm.*

*Figure 4: Dynamic SnO<sub>2</sub> response (conductance G versus time) at 523 K towards increasing O<sub>2</sub> concentration steps in N<sub>2</sub> for two injection cycles.*

*Figure 5: Dynamic SnO<sub>2</sub> response (conductance G versus time) at 623 K towards increasing O<sub>2</sub> concentration steps in N<sub>2</sub>, for 3 injection cycles.*

*Figure 6: Relative response versus injected O<sub>2</sub> concentration in N<sub>2</sub> at 523 K, 623 K and 723 K.*

*Figure 7: Dynamic SnO<sub>2</sub> response (conductance G versus time) at 523 K towards increasing O<sub>2</sub> concentration steps in 4.5 vol% H<sub>2</sub> balanced with nitrogen for three injection cycles.*

*Figure 8: Dynamic SnO<sub>2</sub> response (conductance G versus time) at 623 K, towards increasing O<sub>2</sub> concentration steps in 4.5 vol% H<sub>2</sub>, for 3 injection cycles.*

*Figure 9: X-ray diffraction patterns of the sensing layer after tests at 723 K in 4.5 vol% H<sub>2</sub>.*

*Figure 10: Comparison of relative responses versus O<sub>2</sub> concentrations measured at the outlet of the bench, at various temperatures, either in N<sub>2</sub> or in 4.5 vol% H<sub>2</sub>.*

## Tables captions

*Table 1: Comparison of injected oxygen concentrations (furnace inlet) with outlet ones measured by a SYSTECH probe in N<sub>2</sub> and 4.5 vol% H<sub>2</sub> (gas flow 5 l/h), at various temperatures (293–723 K), without any sensor inside the furnace.*

*Table 2: Comparison of injected oxygen concentrations (furnace inlet) with outlet ones measured by a SYSTECH probe in 4.5 vol% H<sub>2</sub> (gas flow 5 l/h), at various temperatures (293–723 K), without and with sensor inside the furnace*

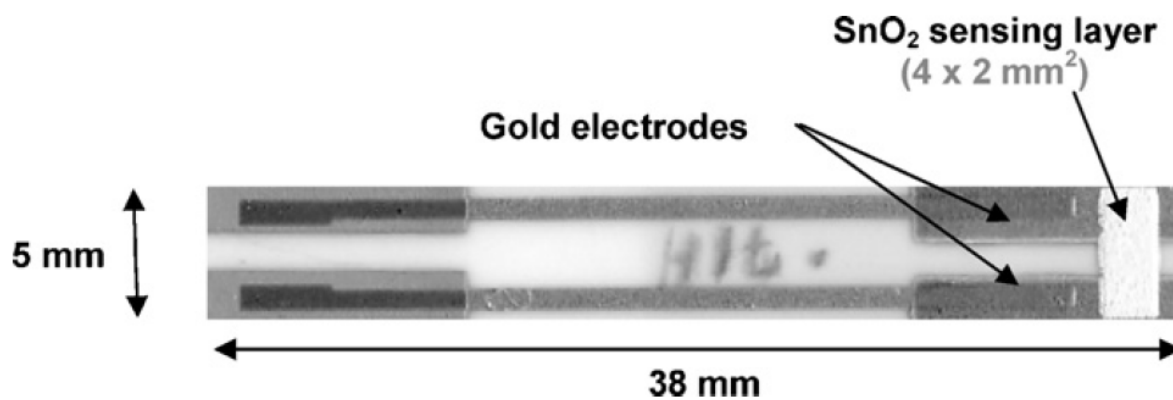


Figure 1

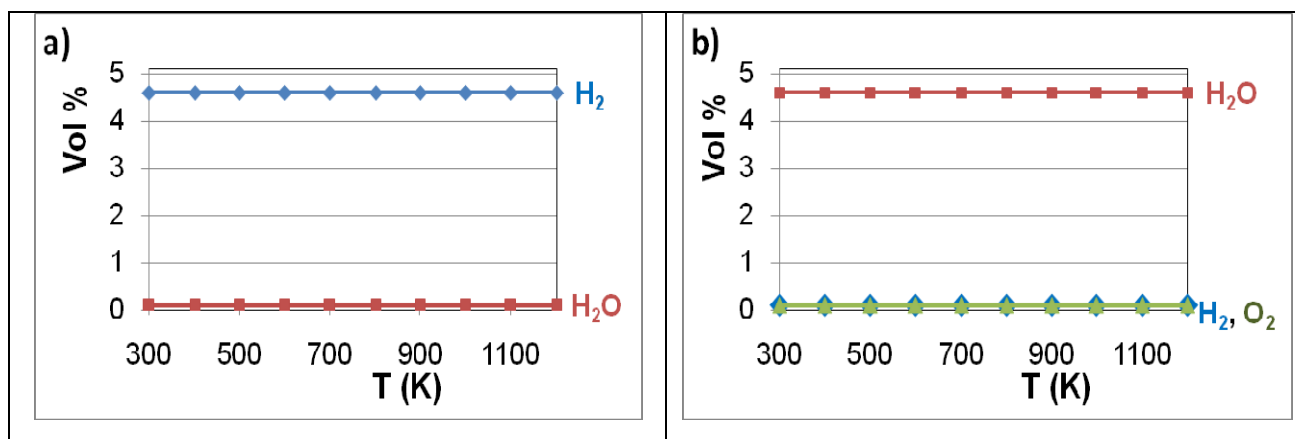


Figure 2

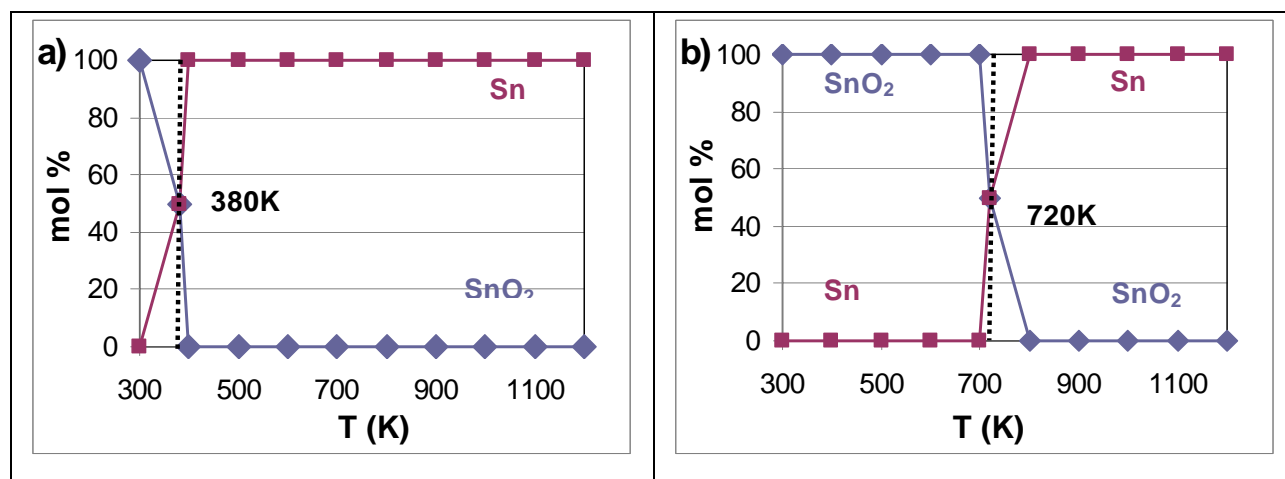


Figure 3



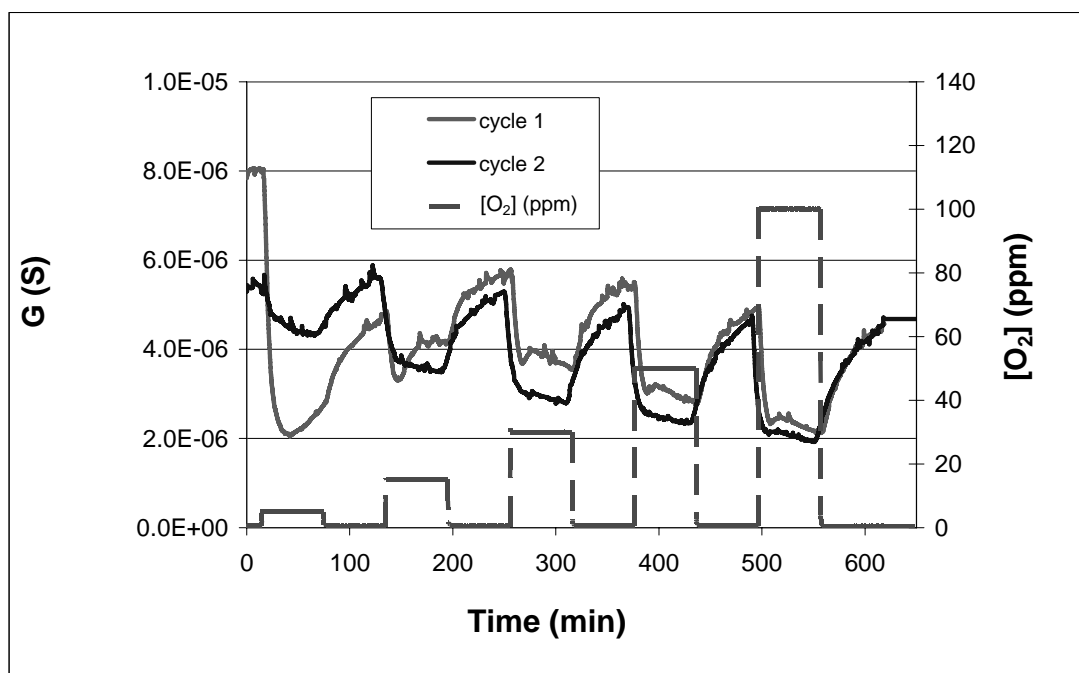


Figure 4

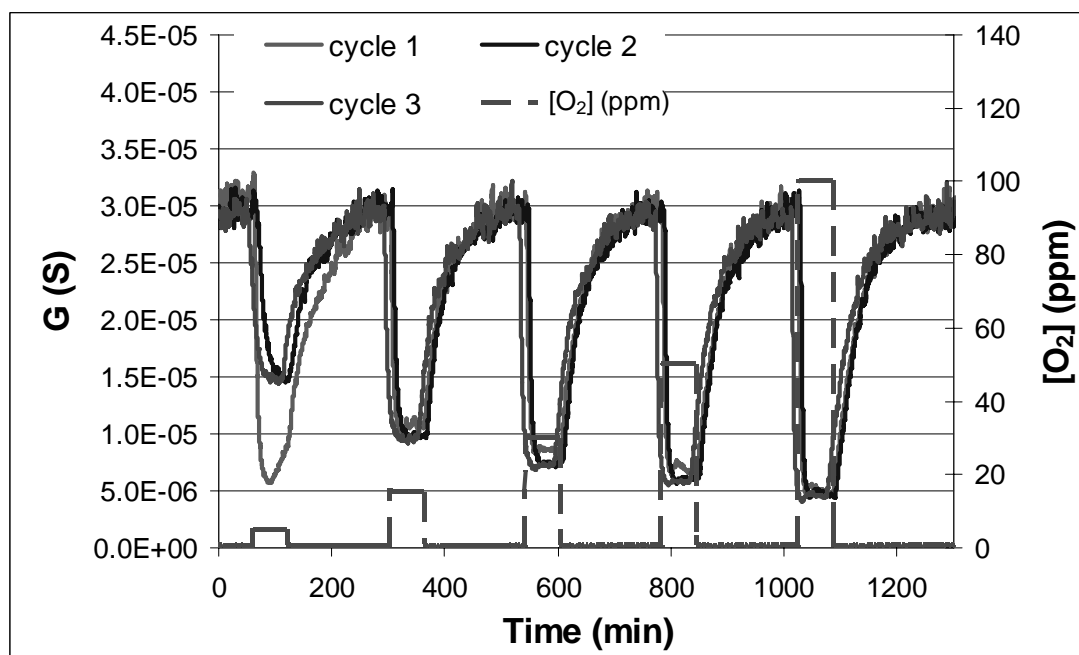


Figure 5

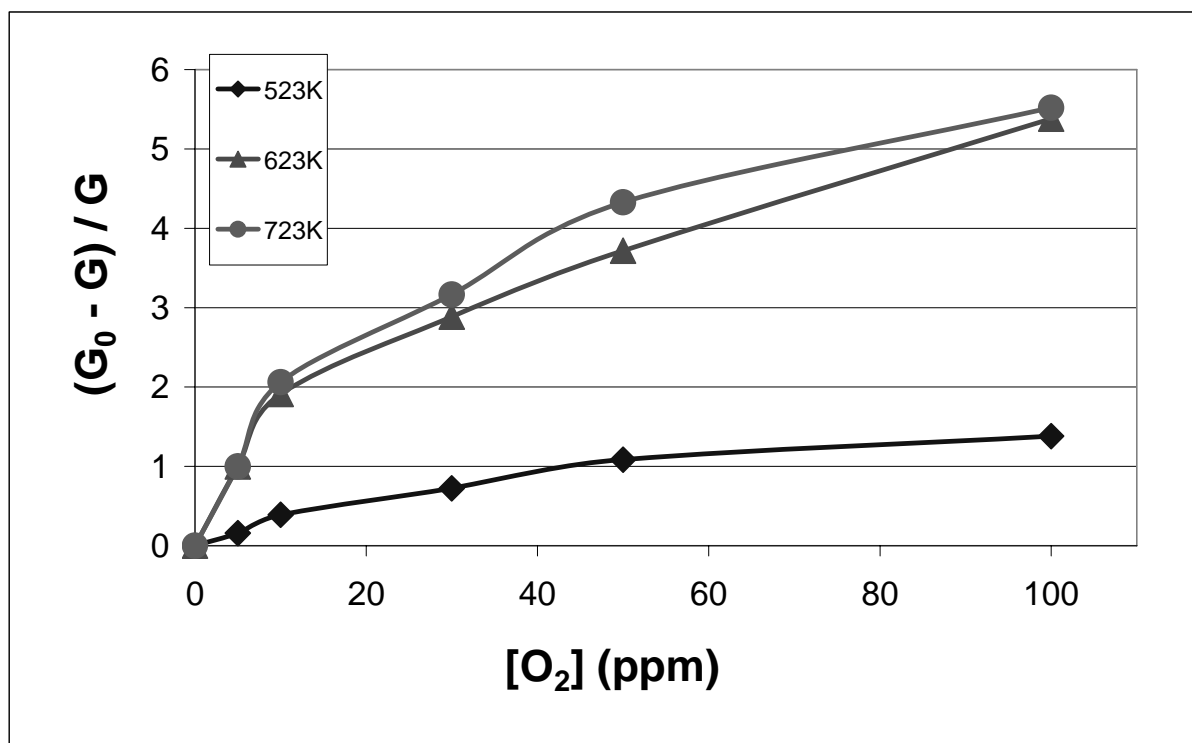


Figure 6

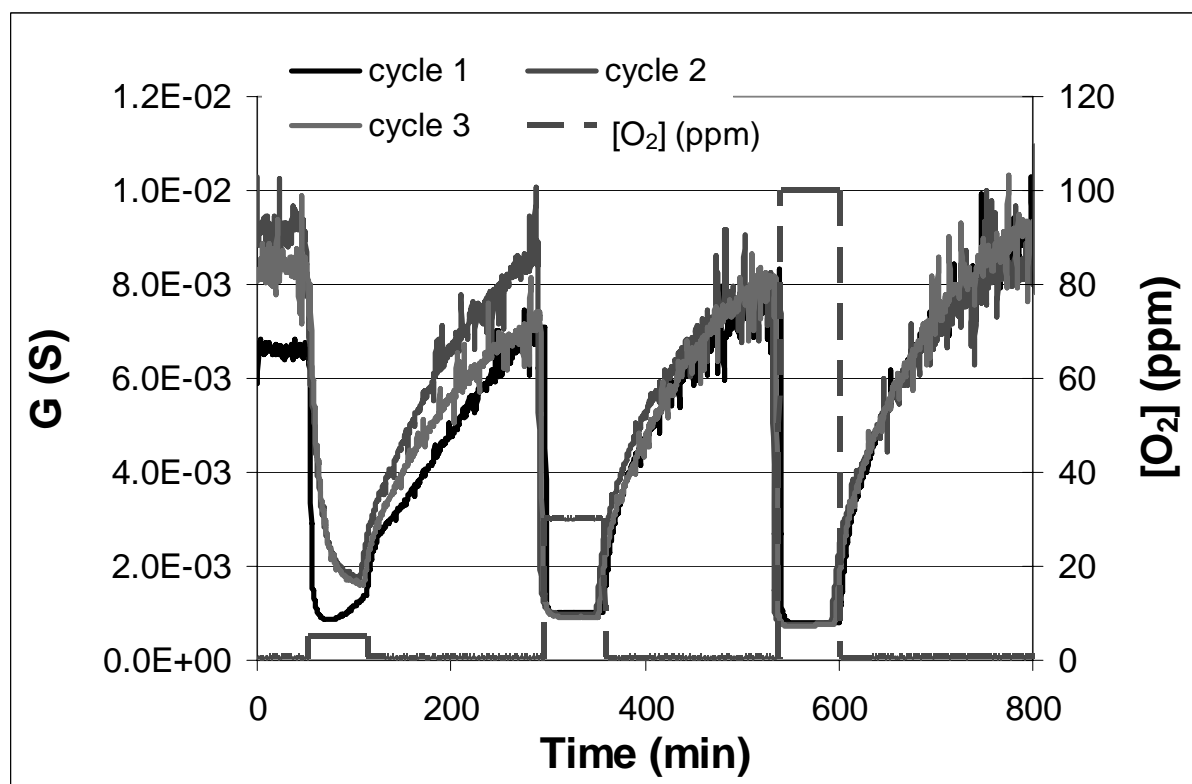


Figure 7

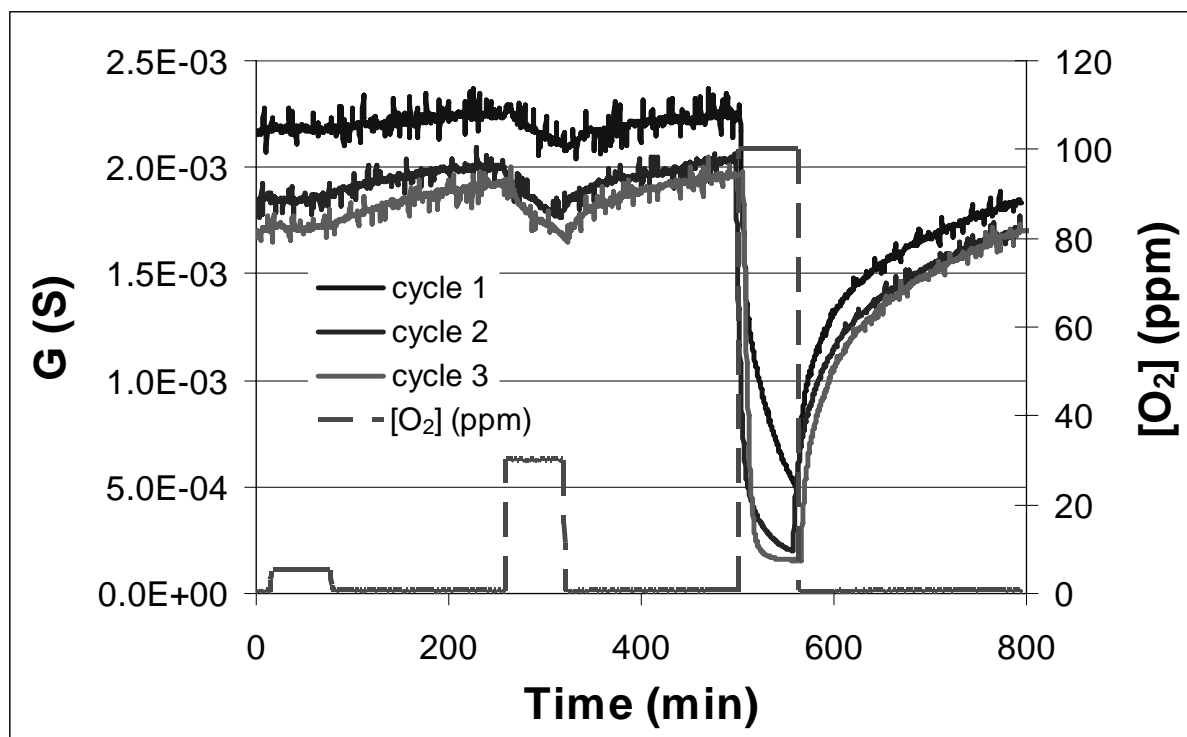


Figure 8

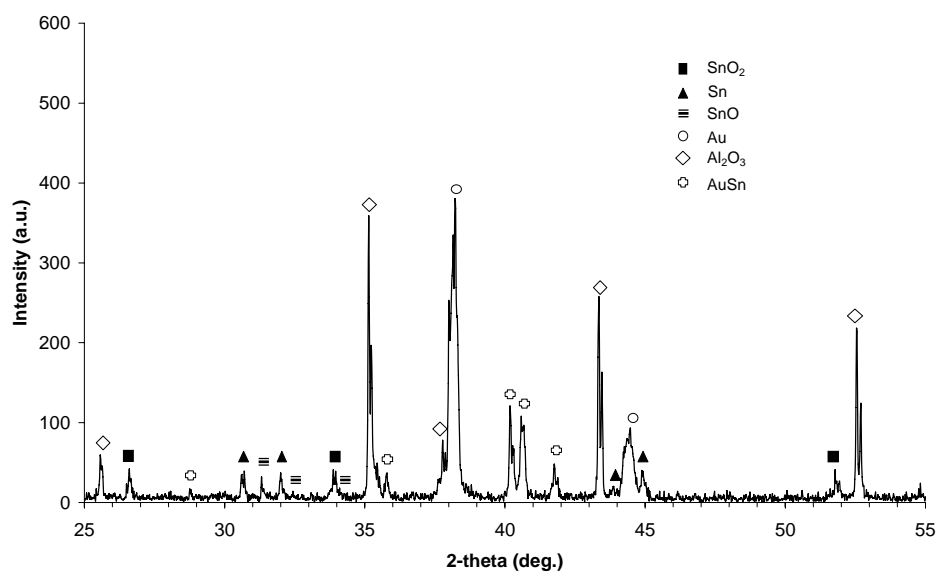


Figure 9

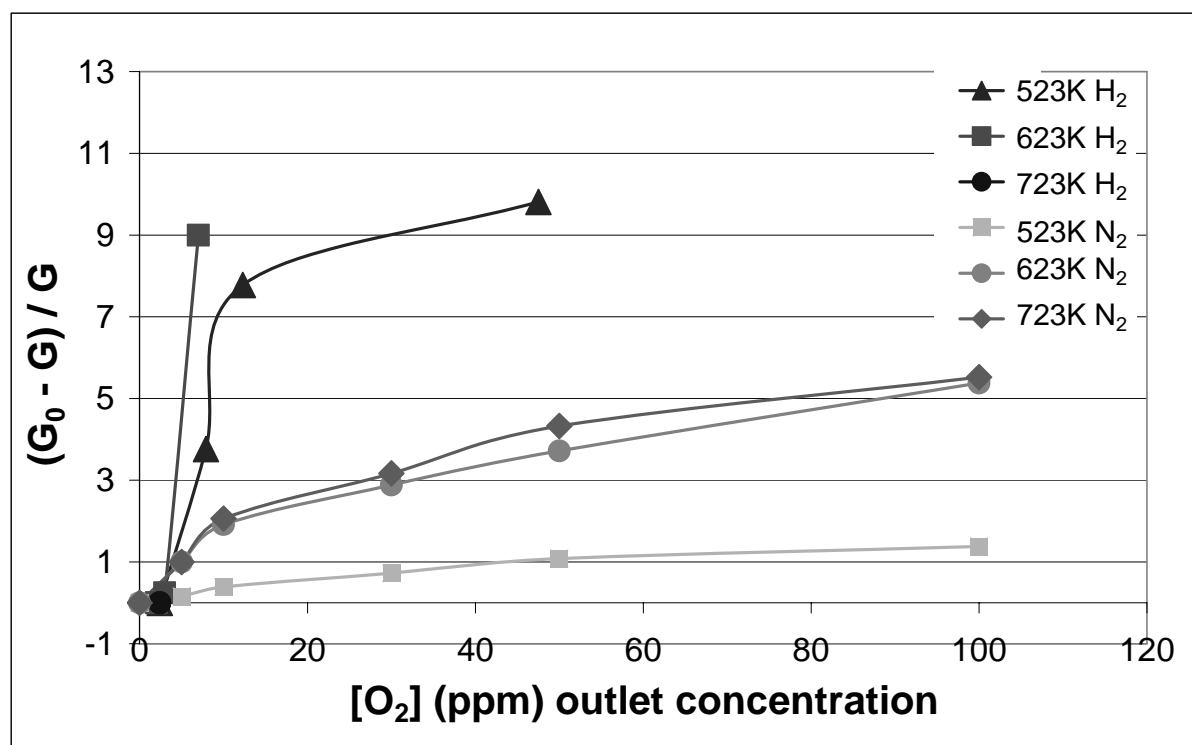


Figure 10

Table 1

T (K)	Gas environment	[O <sub>2</sub> ] (ppm) (without sensor in furnace)	
		Inlet injection	Outlet measurement
293	N <sub>2</sub>	0	6
		5	11
		30	33
		100	98
293	N <sub>2</sub> + 4.5% H <sub>2</sub>	0	5
		5	9
		30	30
		100	97
523	N <sub>2</sub> + 4.5% H <sub>2</sub>	0	4
		5	6
		30	24
		100	81
723	N <sub>2</sub> + 4.5% H <sub>2</sub>	0	4
		5	4
		30	4
		100	4
723	N <sub>2</sub>	100	74 (5 l/h)
		100	91 (12 l/h)

*Table 2*

T (K)	[O <sub>2</sub> ] (ppm)		
	Inlet injection	Outlet measurement WITHOUT sensor	Outlet measurement WITH sensor
523	0	4	2
	30	24	12
	100	81	47
623	0	-	2
	30	-	3
	100	-	7
723	0	4	2
	30	4	2
	100	4	2